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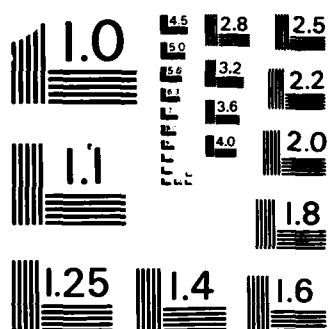
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A HREELS/TDS Study of the Intermediate Formed by the
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A significant body of work is beginning to appear on the chemistry of amines and organic cyanides on single crystal transition metal surfaces in UHV [1-14]. In particular, the thermal chemistry of cyanogen (C_2N_2) adsorbed on single-crystal platinum surfaces has been examined by a number of authors [3-13]. The results from studies on Pt(100) [4-7], Pt(110) [8-10], Pt(111) [11,12], and a stepped Pt surface with Pt(111) terraces [13] show a qualitative insensitivity of C_2N_2 chemistry to the structure of the underlying platinum surfaces. In all cases just cited, cyanogen is the only desorption product observed. In thermal desorption studies, three desorption states are usually observed (α, β_1, β_2). The α state, with desorption temperature in the range 370K [Pt(111)] to 460K [Pt(110)], is believed to arise from molecularly adsorbed C_2N_2 . The β states desorb at much higher temperatures and are often not resolvable. The β_1 state desorbs in the range 680-690K, while the β_2 state desorbs at 750-870K. There is evidence that the presence of strongly-bonded oxygen in the Pt (possibly associated with impurities) has an affect on the β state desorption behavior [14].

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Recent work from this laboratory showed that when H_2 is coadsorbed with C_2N_2 on Pt(111) the α state of C_2N_2 is partially hydrogenated [12]. The partially hydrogenated surface species decomposes to give back $C_2N_2 + H_2$ at $\sim 430K$. Since this temperature is well above the desorption temperature of the C_2N_2 α state from Pt(111) this decomposition results in a sharp C_2N_2 desorption feature. The same desorption feature at 430K is observed in the decomposition of ethylenediamine ($H_2N-CH_2-CH_2-NH_2$) on Pt(111). The thermal decomposition of partially deuterated ethylenediamine ($H_2N-CD_2-CD_2-NH_2$) was used to show that the initial removal of H from the nitrogen atoms occurs before the breaking of the C-D bonds.¹² On the basis of those results we speculated that the intermediate formed by coadsorption of H_2 and C_2N_2 and the decomposition of ethylenediamine is the ethylenedinitrene ($N-CH_2-CH_2-N$). However, it was recognized that the thermal decomposition data was not definitive since a major competing decomposition channel for ethylenediamine results in HCN as product. Also, in the decomposition of $H_2N-CD_2-CD_2-NH_2$ the tail of the hydrogen desorption peak extends up to 430K (the temperature of C_2N_2) evolution. Clearly, spectroscopic identification of the intermediate formed from $H_2 + C_2N_2$ is desirable.

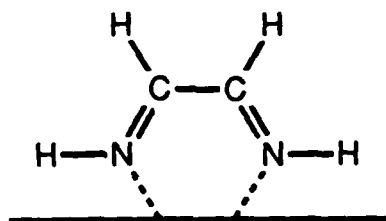
In this manuscript we report HREELS studies of the surface intermediate formed by the coadsorption of H_2 and C_2N_2 . The HREELS data combined with TDS results show that the species formed is indeed a partially hydrogenated species with C-H bonds, and is most likely the diimine species $HN=CH-CH=NH$.

The experiments described here were conducted in an ultra-high vacuum chamber equipped with a 127° single-pass monochromator, single-pass analyzer HREELS spectrometer, a cylindrical mirror analyzer for Auger electron spectroscopy, a quadrupole mass spectrometer used for thermal desorption spectroscopy and an ion gun for sputter cleaning of the sample. The HREELS experiments, TDS experiments and Auger experiments were controlled by an IBM PC computer with Tecmar Labmaster interface board. The Pt crystal was spark cut from a Pt rod obtained from AREMCO. The surface orientation was within 2° of the (111) surface. The crystal was cleaned by standard procedures of Ar^+ ion bombardment, oxygen treatments and annealing [12,14].

Figure 1a shows the thermal desorption spectrum of C_2N_2 following adsorption on the clean Pt surface. The α and β states are clearly recognized. The α state desorption occurs at 360K. Figure 1b shows the C_2N_2 thermal desorption following coadsorption of 10 Langmuir H_2 and 0.3 Langmuir of C_2N_2 . The α state has been completely replaced by the new state at 430K. The new state at 430K corresponds to the decomposition of the surface species which is the subject of this manuscript. The TDS results shown in Figure 1 are in complete agreement with earlier results in the literature [9].

Figures 2a and 2b show the HREELS spectra obtained following the coadsorption of H_2 and C_2N_2 (figure 2a) and D_2 and C_2N_2 (figure 2b) at 273K. Three loss peaks are evident in the $\text{H}_2 + \text{C}_2\text{N}_2$ spectra, at 1450 cm^{-1} , 1560 cm^{-1} and 3350 cm^{-1} . The peak at 3350 cm^{-1} is thought to be overlap of the C-H and N-H stretch

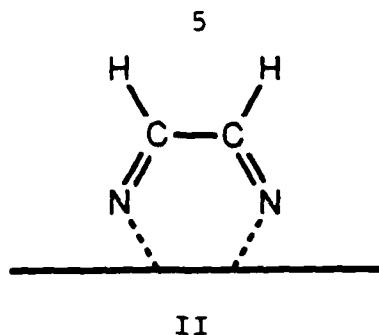
modes. This frequency is too high to correspond to a $\text{N-CH}_2\text{-CH}_2\text{-N}$ species which should have a C-H stretch at $\sim 2900\text{-}3000\text{ cm}^{-1}$. However, it would fit well with a NH=CH-CH=NH species (a di-imine). The modes at 1450 cm^{-1} and 1560 cm^{-1} are taken to be the H-CN bend and the C=N stretch respectively. Since these modes are observed to be close in frequency, it is expected that they will be heavily mixed. The C=N stretch frequency of $\sim 1560\text{ cm}^{-1}$ would correspond to a CN bond order slightly below 2. A possible structure consistent with the spectra in figure 2a is:



I

Figure 2b shows the spectra obtained from $\text{D}_2 + \text{C}_2\text{N}_2$ coadsorption. The C-D mode is observed at 2460 cm^{-1} and the C=N stretch has shifted to 1450 cm^{-1} . The D-CN bending vibration is believed to be shifted to low enough frequency so that it is obscured by the tail of the elastic beam in these experiments.

Since we do not expect to be able to resolve the CH and NH stretch modes of a di-imine species we do not have direct evidence of the existence of NH bonds in the surface intermediate. Thus a species such as II would also match our spectroscopic evidence.



We favor the di-imine structure (I) since it is a known, stable, ligand in several organometallic complexes.¹⁶ Careful spectroscopic studies of the decomposition of the deuterated ethylenediamines ($\text{NH}_2\text{CD}_2\text{CD}_2\text{NH}_2$, $\text{ND}_2\text{CH}_2\text{CH}_2\text{ND}_2$) may shed light on this point. Experiments along this line are underway at present but initial results indicate that they are complicated by the coexistence of multiple species on the surface.

It should be pointed out that the spectra of figure 2 could also be obtained from a side-bonded HCN species in which the CN bond order was reduced due to the interaction with the Pt. This model can be ruled out, however, based on the TDS results following direct adsorption of HCN on Pt(111). When HCN is adsorbed on Pt(111), thermal desorption experiments produce C_2N_2 desorption but only in the β states at temperatures above 600K [3]. HCN adsorption on Pt(111) does not produce any surface species which leads to C_2N_2 desorption at 430K (the decomposition temperature of the surface intermediate of interest here).

To show that the HREELS spectra of Figure 2 indeed correspond to the surface intermediate in question (which decomposes at 430K) we have followed the temperature dependence of the spectra. In these experiments D_2 and C_2N_2 were coadsorbed at ~220K. Initial HREELS spectra at that temperature showed no evidence of the intermediate. A series of annealing experiments were then

carried out. The sample was rapidly warmed to a higher temperature, held there for 10 seconds, and then allowed to cool back to 220K at which time another spectra was obtained. This was carried out for successively higher annealing temperatures. Figure 3a shows that the intermediate begins to form at $\sim 250\text{K}$ and the reaction is complete by 273K. Figure 3b shows another set of spectra starting with adsorption at 273K and annealing to higher temperature. The intermediate appears to be stable to near $\sim 410\text{K}$ at which point decomposition appears to have started. The intermediate is completely gone by $\sim 430\text{K}$. This corresponds well with the TDS behavior shown in figure 1b.

The HREELS and TDS data indicate that a surface intermediate is formed when H_2 and C_2N_2 are coadsorbed on Pt(111). The intermediate is a partially hydrogenated species in which one hydrogen has been attached to each carbon and nitrogen of the C_2N_2 . The di-imine species is formed at $\sim 250\text{K}$ and decomposes to give back $\text{C}_2\text{N}_2 + \text{H}_2$ at $\sim 430\text{ K}$. This intermediate is also observed as the final step in one channel of the dehydrogenation of ethylenediamine on Pt(111) [12]. It is important to point out the complementary nature of the HREELS and TDS results. The HREELS data by itself cannot be used to rule out surface HCN as the intermediate. However, the TDS results clearly rule this out.

Acknowledgments:

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Figure Captions

Figure 1 Thermal desorption spectra monitoring mass 52 intensity vs sample temperature. (a) following a 0.3 Langmuir exposure of C_2N_2 to a clean Pt surface. (b) following exposure of 0.3 Langmuir of C_2N_2 to a Pt surface which had been preexposed to 10. Langmuir H_2 .

Figure 2 HREELS spectrum obtained after coadsorption of (a) H_2 and C_2N_2 and (b) D_2 and C_2N_2 at 273K. In each case a preexposure of 10. Langmuir H_2/D_2 was followed by an exposure of 0.3 Langmuir C_2N_2 .

Figure 3 HREELS spectra following successively higher surface annealing temperatures. The spectra in (a) were obtained at 220K following adsorption at 220K and annealing to the indicated temperature. The spectra in (b) were obtained at 273K following adsorption at 273K and annealing to the indicated temperature.

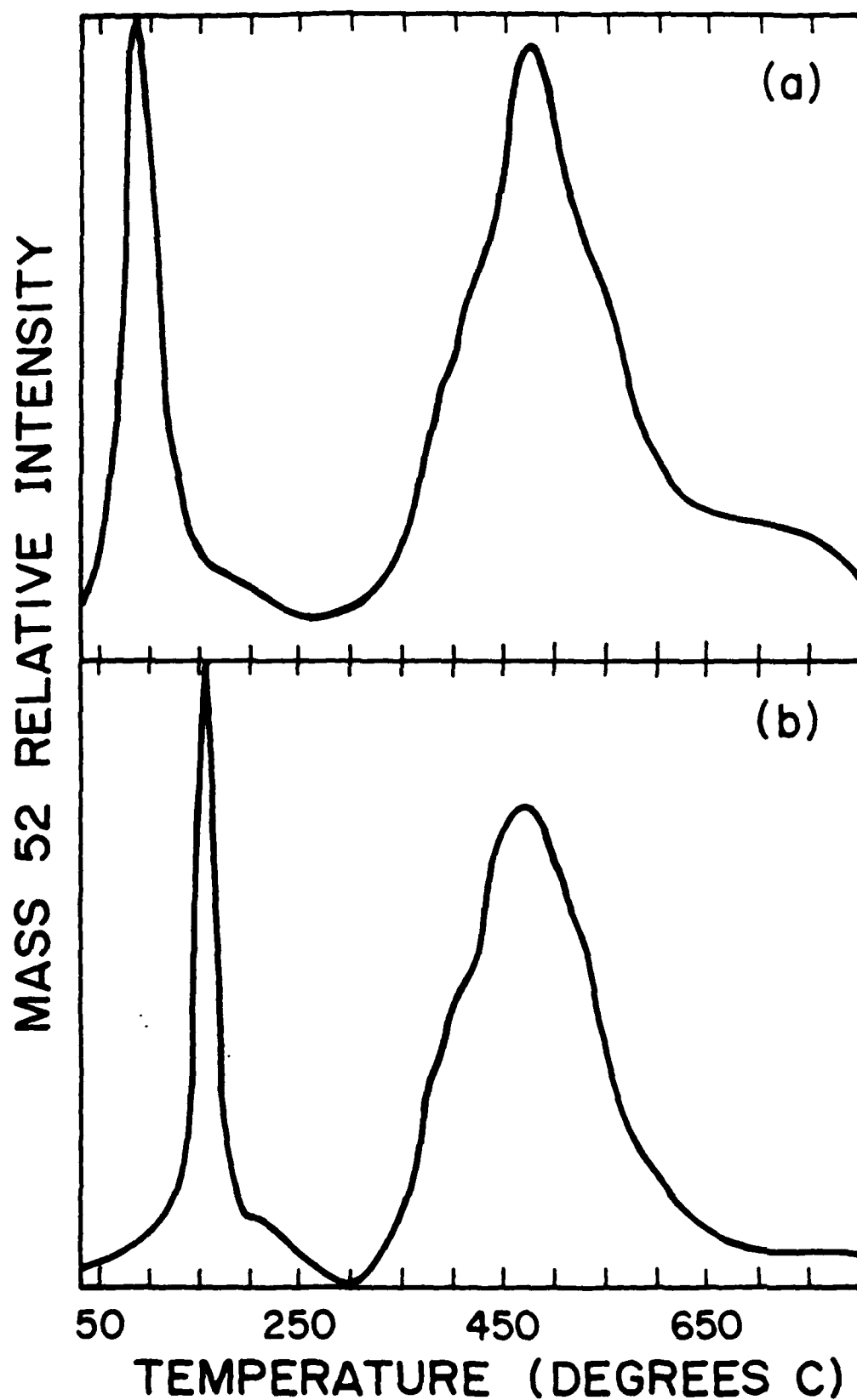


Figure 1

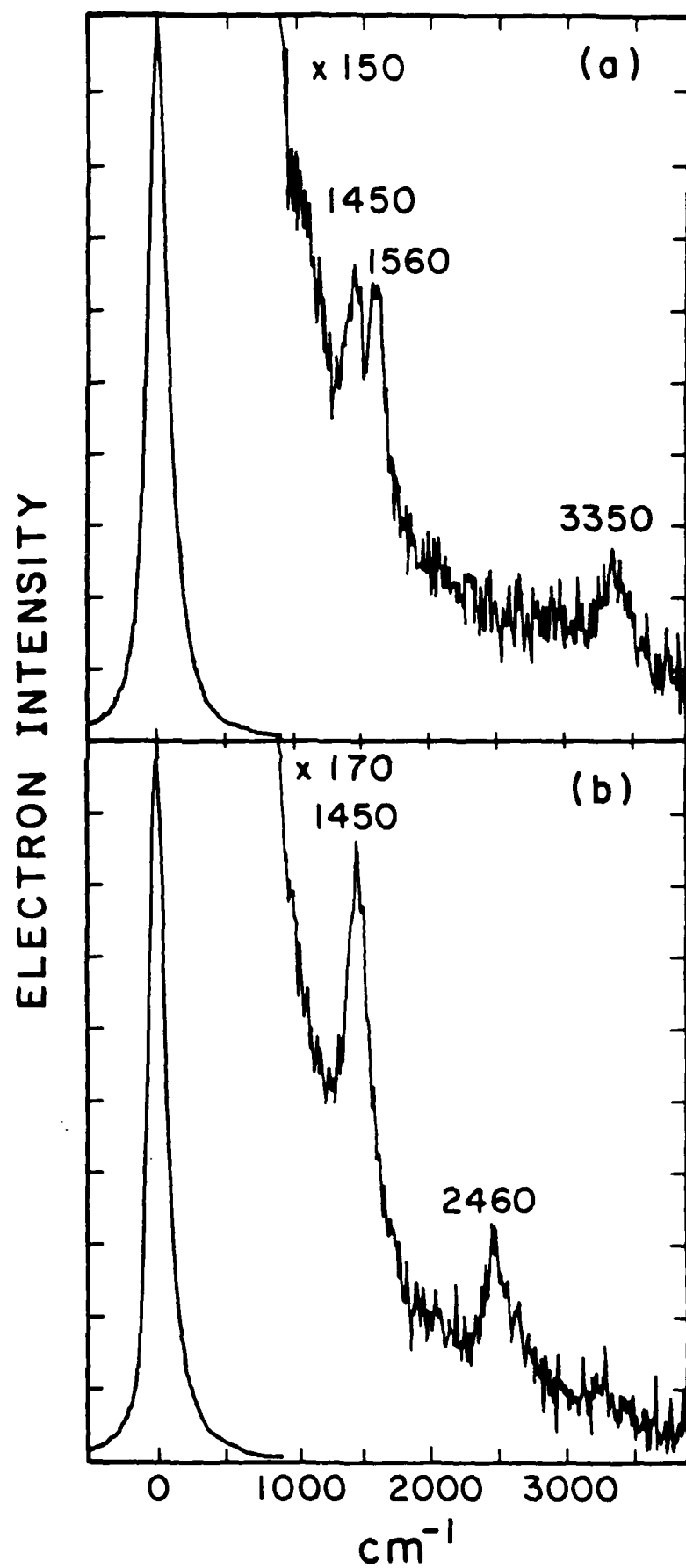


Figure 2

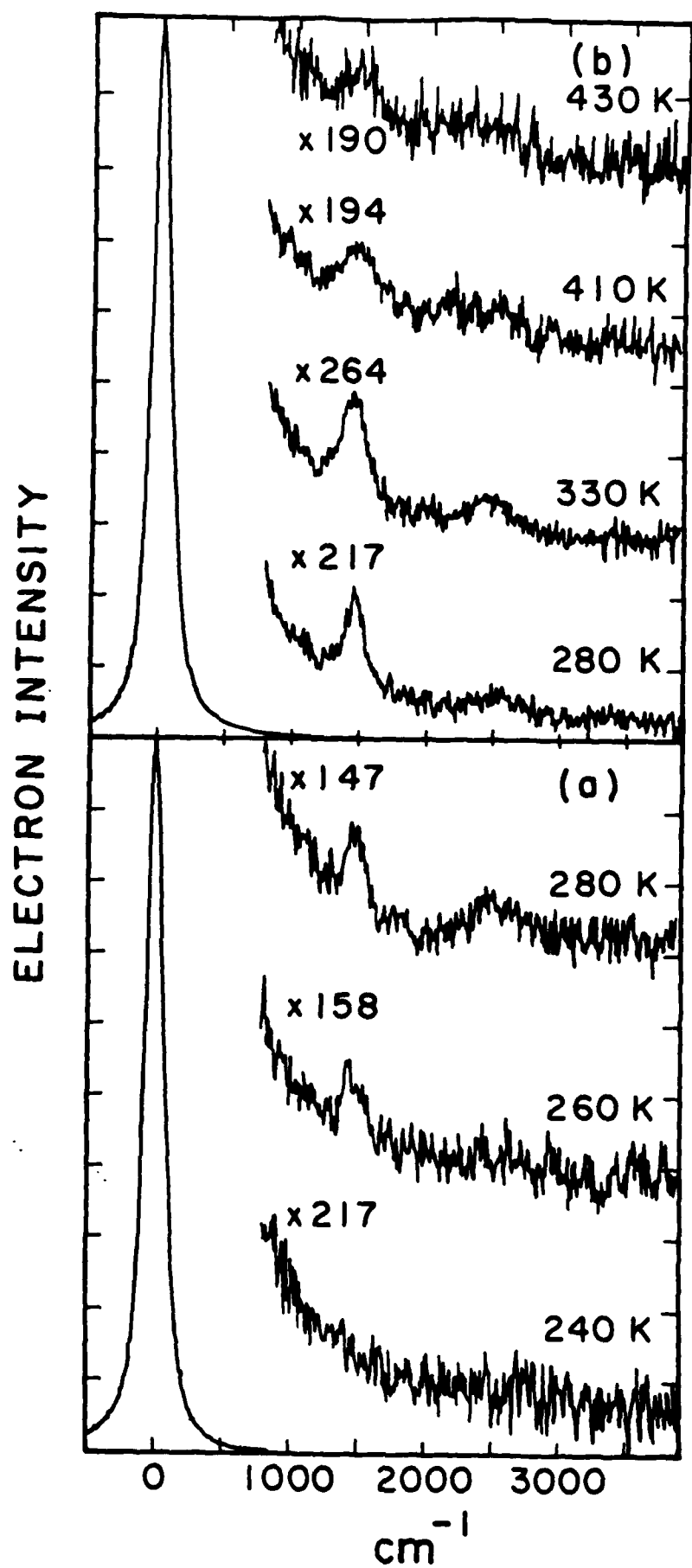


Figure 3

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